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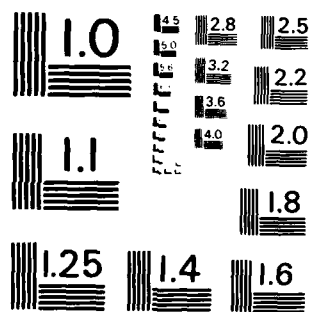
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STUDY OF SINGLET OXYGEN-PENTAVALENT PHOSPHORUS REACTIONS

FINAL REPORT

STUDY OF SINGLET OXYGEN-PENTAVALENT PHOSPHORUS REACTIONS

FINAL REPORT

AFOSR-TR. 84-0499

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Detailed studies of an atomic oxygen-singlet delta oxygen-dimethyl hydrogen phosphite gas phase reaction system have been performed. Decay of singlet delta oxygen was modeled and a reaction mechanism which explains the experimental observations was derived.

Semilog plots of oxygen singlet delta emission intensities versus time obtained show an initial rise in the emission followed by a straight line decay. The mechanism that best explains this is reaction of oxygen atoms with the phosphorus compound to form an intermediate species which quenches the oxygen singlet delta. Emission from the intermediate species explains the initial rise in intensity.

It was also found that nitric oxide terminates the quenching of oxygen singlet delta, presumably by reaction of nitric oxide with the phosphorus intermediary. Addition of water to the flow resulted in no change in singlet delta emission time history. This indicates that oxygen singlet delta does not enhance the hydrolysis of the studied phosphorus compounds.

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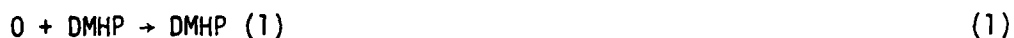| 22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
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1. SUMMARY

Detailed studies of an atomic oxygen-singlet oxygen-dimethyl hydrogen phosphite (DMHP) gas phase reaction system have been performed. Decay of singlet delta oxygen was modeled and a reaction mechanism which explains the experimental observations was derived. —

Semilog plots of O_2 singlet delta emission intensities in the presence of O-atoms and DMHP versus time obtained show an initial rise in the emission followed by a straight line decay. The mechanism that best explains this is the following:

$$O + DMHP \rightarrow DMHP~(1) \tag{1}$$

$$DMHP~(1) + O_2(^1\Delta) \rightarrow DMHP~(1) + O_2 \tag{2}$$

$$DMHP~(1) + O_2(^1\Delta) \rightarrow DMHP~(2) + O_2 \tag{3}$$

$$DMHP~(2) \rightarrow DMHP~(1) + h\nu \tag{4}$$

The reaction sequence is initiated by the reaction of oxygen atoms with the phosphorus compound. This forms a species, designated by DMHP (1), which quenches singlet delta oxygen forming ground state O_2 and leaving either the original DMHP (1) or a second species, designated as DMHP (2), which then radiates in the singlet delta region. This leads to observed enhancement of the singlet delta emission. Spectroscopy of the emission upon addition of the phosphorus compounds to the flow indicated that there was indeed a broadband emission due to the phosphorus. It was possible to derive a set of reaction rate constants that fit the experimental data. It was also found that NO terminates the quenching of $O_2(^1\Delta)$, presumably by reaction with the DMHP (1) intermediary via

$$DMHP~(1) + NO \rightarrow products. \tag{5}$$

Addition of water to the flow tube did not change the quenching rate of the oxygen singlet delta, indicating that the hydrolysis of the phosphorus compound was very slow in comparison to the reaction of water with the phosphorus compound.

2.0 RESEARCH OBJECTIVES

The major objective of this effort was to experimentally characterize the reactions of excited oxygen singlet delta with pentavalent phosphorus compounds. The compounds selected had structures and chemical bonds similar to those found in the nerve agents. Phosphonate esters were chosen as the most likely candidates because they are structurally similar with and -OR group replacing an -F group. The emphasis was to determine if singlet delta oxygen could be used as an energy source to cause decomposition or hydrolysis of pentavalent phosphorus compounds, leading to products that could have significantly reduced bioactivity. The experimental study included investigation of the reaction kinetics, determination of the reaction mechanisms, and identification of reaction products. This involved designing an appropriate experiment, developing and calibrating necessary diagnostics to characterize the experiment, taking of data and development of a kinetic model to characterize the data.

3. RESEARCH EFFORT

3.1 APPARATUS AND DIAGNOSTICS

Two flow tubes were used to perform the reaction studies. The one used in the initial studies is illustrated in Figure 1. Oxygen atoms and singlet oxygen are produced through a microwave discharge through molecular oxygen. For some experiments, a chemical generator was used to provide the singlet oxygen. This produced larger densities of singlet oxygen than the microwave, with no O atoms. The second flowtube is shown in Figure 2. This flowtube had three observation positions with ZnSe broadband AR coated windows as well as sampling ports downstream of the flowtube mixer to allow reaction product collection.

The microwave discharge source of singlet oxygen is provided by oxygen flow through an Evenson-Broida cavity. Oxygen flows of 0.1 to 0.20 mmoles/sec can be delivered at the flowtube entrance, containing typically 5 percent oxygen singlet delta. The phosphorus compounds to be studied are introduced into the flow through a mixer. The P-compound delivery system is illustrated in Figure 3. Nitrogen carrier gas is bubbled through a controlled temperature bath of the phosphorus compound. By controlling the bath temperature and the relative fraction of N_2 carrier gas that passes through the sample, the P-compound flow rate may be selected. This flow system was calibrated for each compound by weight differential. The P-compounds that were studied are listed in Table 1. The majority of the studies were performed with DMHP.

The major diagnostic used in the experiments was emission of the oxygen singlet delta at 1.27 microns. A bandpass filter peaked at 1.27 microns with a bandwidth of 80 angstroms was used with a cooled germanium detector. The detection system was calibrated against EPR measurements of singlet delta oxygen at the Air Force Weapons Laboratory. In addition, the emission around 1.27 microns was scanned using a monochromator equipped with a germanium photomultiplier tube.

The oxygen atom concentration in the experiment was measured and controlled by the titration reactions:
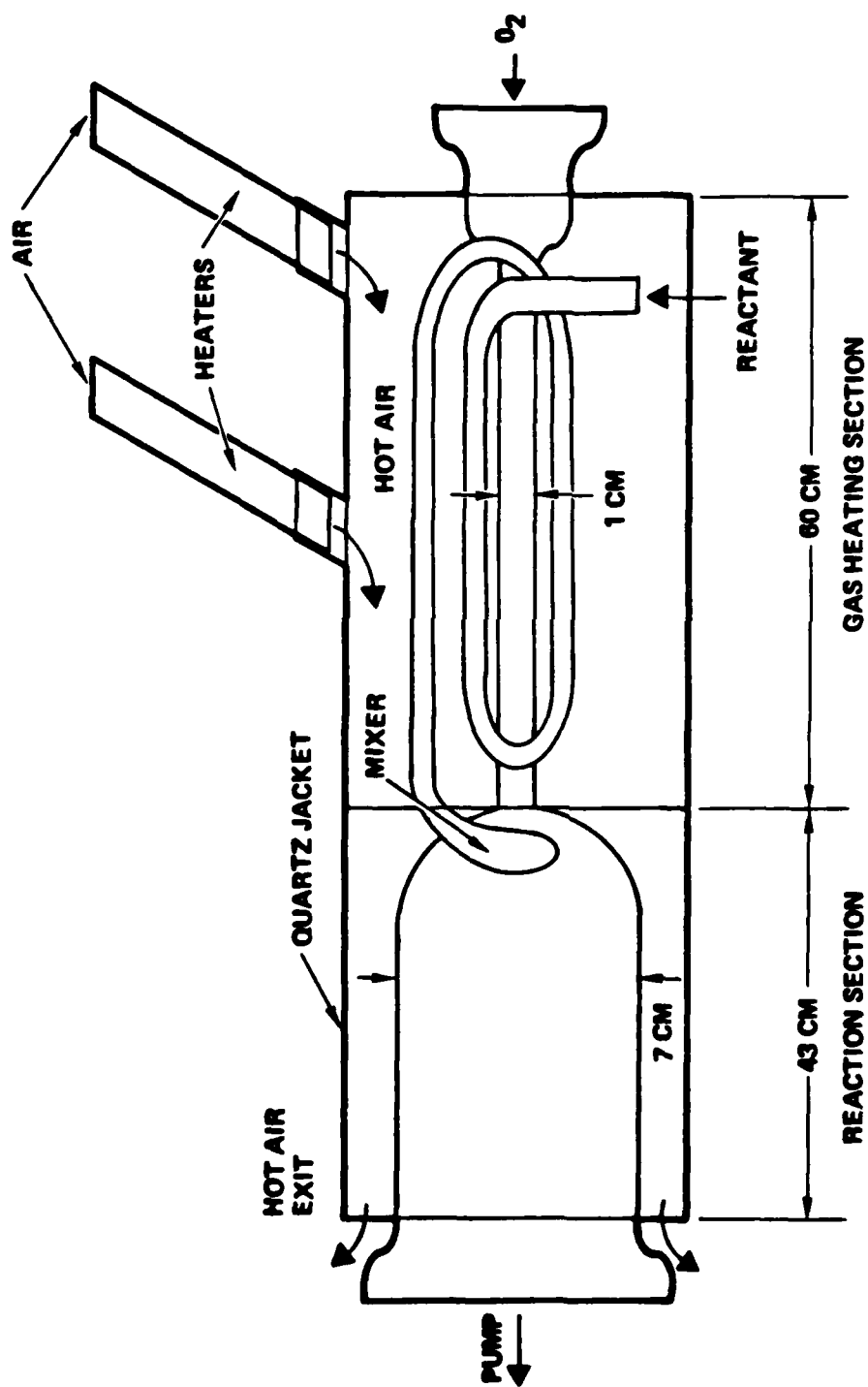
3

Figure 1. Original Flowtube used for Oxygen Singlet
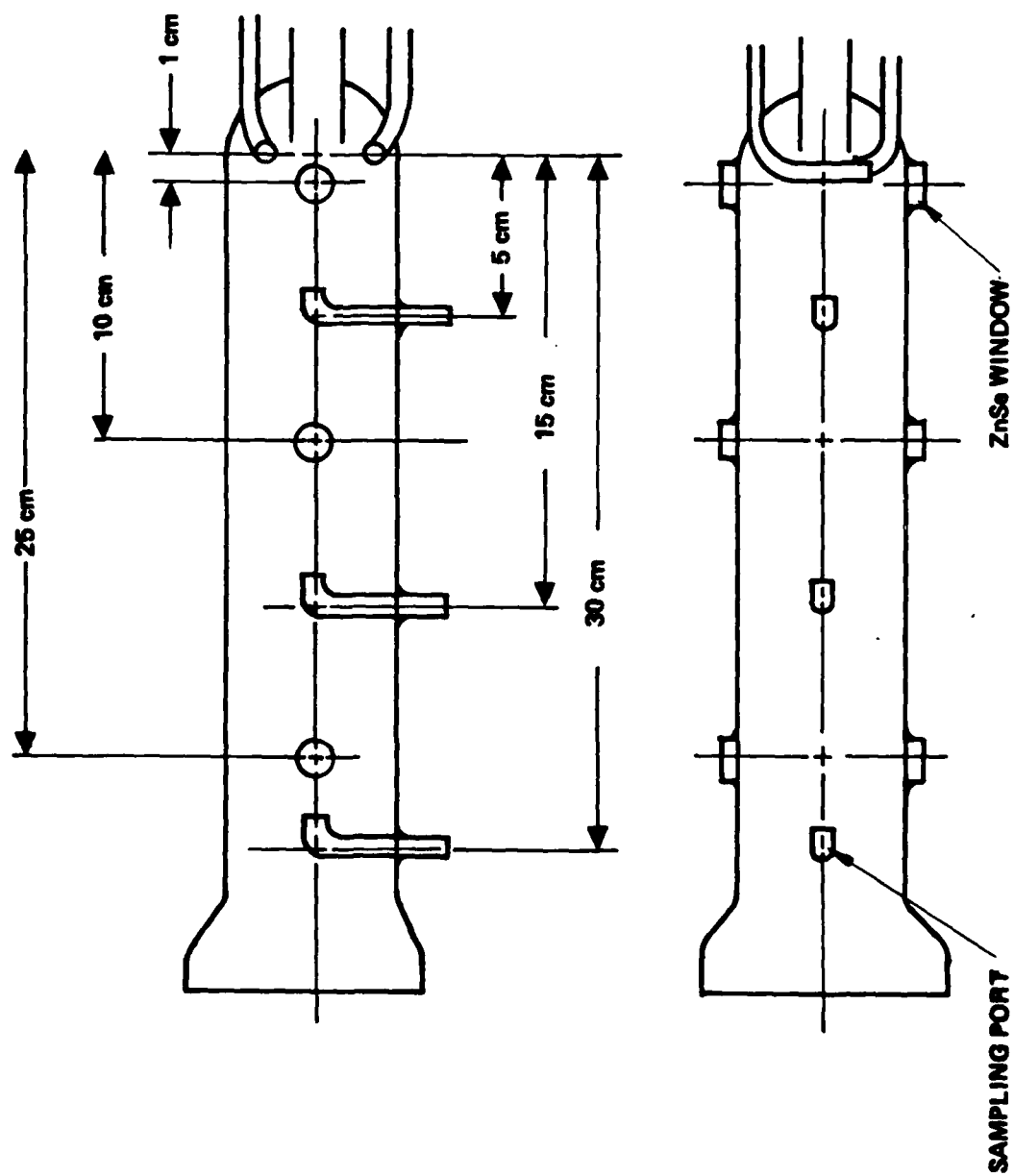Delta-phosphorous Compound Studies.

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Figure 2. Improved Flow Tube Apparatus.

SONIC
FLOW
CONTROLLERS

TO
FLOW TUBE
MIXER

PRESSURE
GAUGE

TEMPERATURE
BATH

PHOSPHOROUS
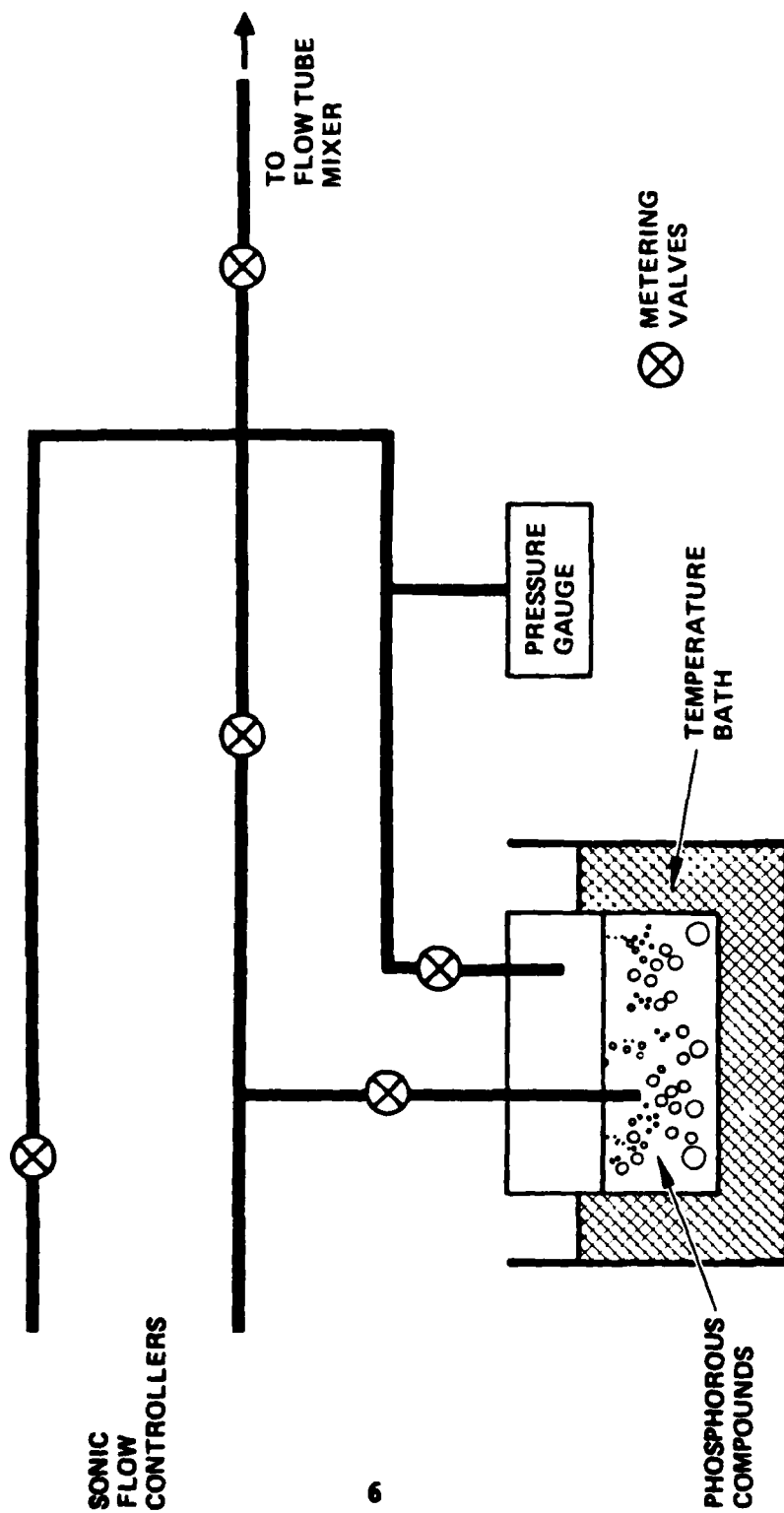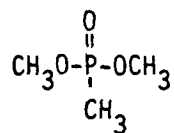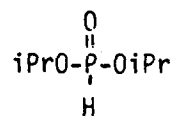COMPOUNDS

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Figure 3. Phosphorus Compound Delivery Apparatus
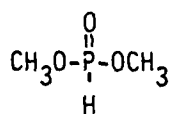
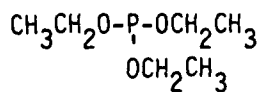TABLE 1.   PHOSPHORUS COMPOUNDS INVESTIGATED

Dimethylmethyl Phosphonate
(DMMP)

$$CH_3O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}-OCH_3$$

Diisopropyl Phosphite
(DIHP)

$$iPrO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OiPr$$

Dimethyl Phosphite
(DMHP)

$$CH_3O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OCH_3$$

Triethyl Phosphite
(TEP)

$$CH_3CH_2O-\underset{\underset{\displaystyle OCH_2CH_3}{|}}{P}-OCH_2CH_3$$

$$O + NO_2 \rightarrow NO + O_2 \qquad\qquad (6)$$

which has a reaction rate of 9×10^{-12} cm^3/molecule-second and a half
life of 10^{-3} second under experimental conditions and

$$NO + O \rightarrow NO_2 + h\nu \qquad\qquad (7)$$

which has a rate of 4×10^{-18} cm^3/molecule-second and a half life of
36 minutes under experimental conditions. A calibrated NO_2 flow rate is
added to the flowtube just beyond the discharge and well before the mixer.
The broad emisison (400-600 nm) was monitored with a photomultiplier/
interference filter (500 nm) 10 cm downstream of the NO_2 injection point
and 15 cm upstream of the mixer. The equivalence point is clearly defined
by the contraction of the broad emission to within a few centimeters of
the NO_2 addition region. The presence of ozone could be ruled out by
the nature of the emission. When NO_2 was used to control the O atom
concentration in the flow system, O-atom concentration is determined by
the difference in NO_2 added to the flow tube and the amount of NO_2 necessary
for complete titration at a given set of microwave discharge conditions.
This allowed precise control of the relative amount of O atoms in a series
of experiments. It was later found that the presence of NO interfered with
the phosphorus reactions. Thus, in some experiments the oxygen atom con-
centration was changed by detuning the microwave discharge.

The phosphorus compound concentration was monitored in some experiments
using a CO_2 laser to measure the absorption of the P-O-C bond at 9.603
microns. Absorption coefficients for the separate phosphorus compounds
were measured and are summarized in Table 2. A single pass phosphorus
absorption measurement in the flow tube showed 1% maximum absorption
which was inadequate for precise measurements. Consequently, a resonant
cavity absorption technique was developed to overcome the sensitivity
problem. The apparatus used for this diagnostic is illustrated in Figure 4.
The technique proved more useful in verifying the flow rate of phosphorus
compound than in kinetic measurements because reaction products absorb in
the same spectral region.

The purity of the P-compounds and the composition of the reaction
products were determined using gas chromatography and IR spectrometry. Samples

	Wavelength CO_2 Line λ (μ)	T = 21°C Vapor Pressure (Torr)	Absorbance 9.4 cm I/I_0	Absorption Coefficient α (Torr^{-1} cm^{-1})
DMMP	9.5265	0.6949	0.674	.064
DMHP	10.1782	1.87	.535	.038
	10.2156	1.86	.725	.019
DIHP	10.2280	.604	.624	.008
	10.3260	.632	.776	.045
TEP	9.6465	2.40	.179	.0806
	9.5775	2.40	.178	.0809

TABLE 2.   LASER ABSORPTION DATA
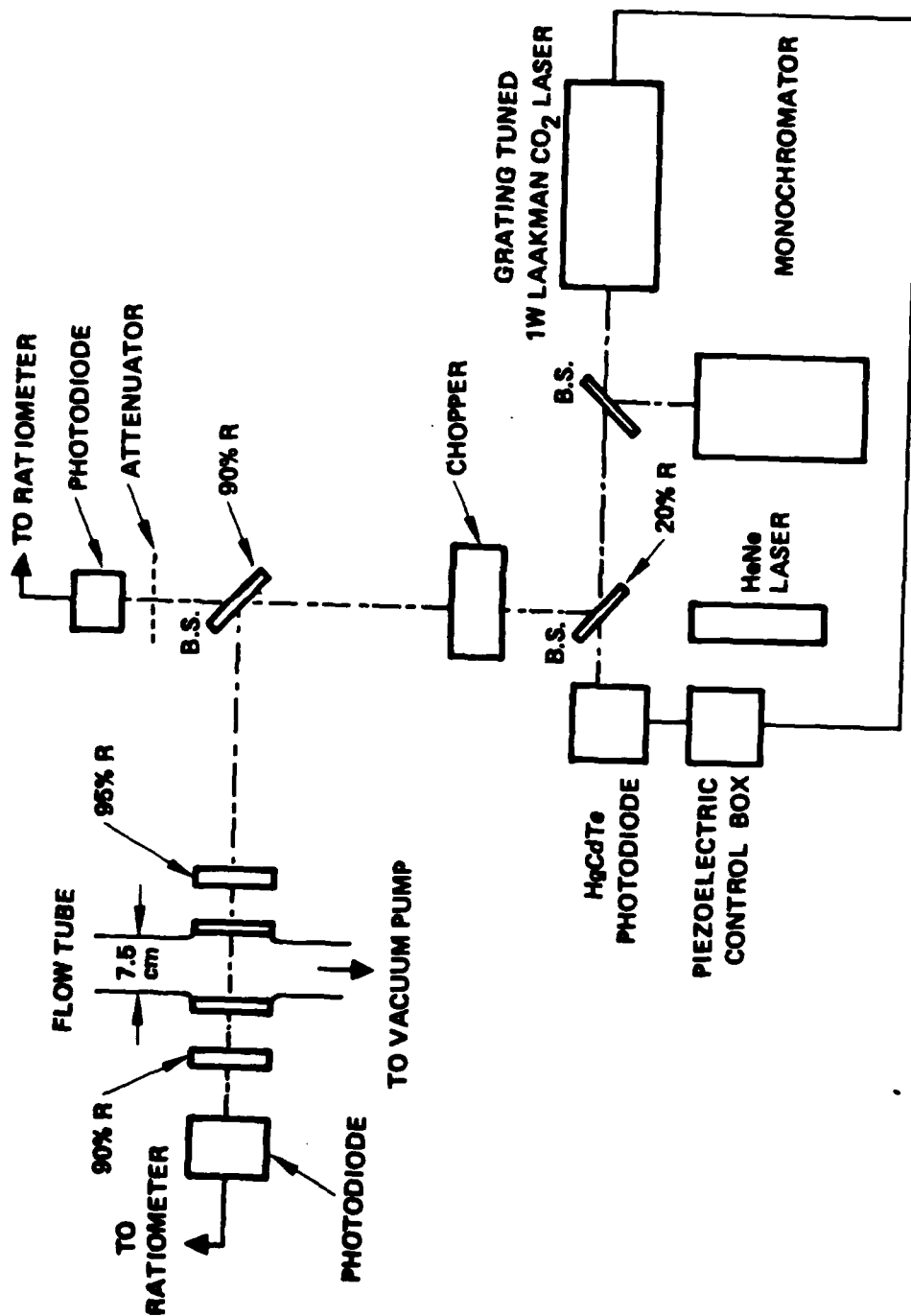
Figure 4. Resonant Cavity CO_2 Laser Absorption Apparatus for Phosphorous Compound Detection.

of reaction products were collected through smapling ports located along the flowtube. They were analyzed with a Hewlett-Packard 5790A gas chromatograph to determine their composition. Infrared spectra were also taken of these samples.

3.2 EXPERIMENTAL RESULTS

Initial phosphorus experiments were performed using microwave generated singlet oxygen and the phosphorus compounds DIHP, DMMP, DMHP, and TEP. Typical results of the O_2 singlet delta reaction with DMHP in the presence of O atoms are shown in Figures 5 and 6. These graphs show semilog plots of O_2 singlet delta versus time. When DMHP is added to the flow there is an initial increase in the 1.27 micron emission followed by a linear decay of the emission. For a given concentration of the phosphorus compound, the increase of the 1.27 micron emission is correlated to the increase in the initial concentration of O atoms. Mechanisms which cause this effect will be discussed in section 3.3. A summary of the data with DMHP is given in Table 3. The oxygen singlet delta decay rate is dependent on the initial DMHP and O-atom concentrations when either is a limiting species. Similar plots using DIHP and DMMP were similar with the decay rates being only weakly dependent on flowtube pressure and initial concentration of the phosphorus compound. The plots of oxygen singlet delta versus time with TEP are shown in Figure 7. The slopes of these plots show a strong dependence upon the flow tube pressure. TEP is trivalent while the other compounds are pentavalent which implies that it would undergo different chemistry.

A separate series of experiments was performed using chemically generated oxygen singlet delta. This provides an oxygen singlet delta concentration that is much higher than the initial phosphorus concentration. There was essentially no change in the decay of singlet delta oxygen when P-compounds are added to the flow (Figure 8). However, the addition of microwave generated oxygen singlet delta to chemically generated oxygen singlet delta and phosphorus compounds produces the same reaction rate present in the initial microwave experiments.
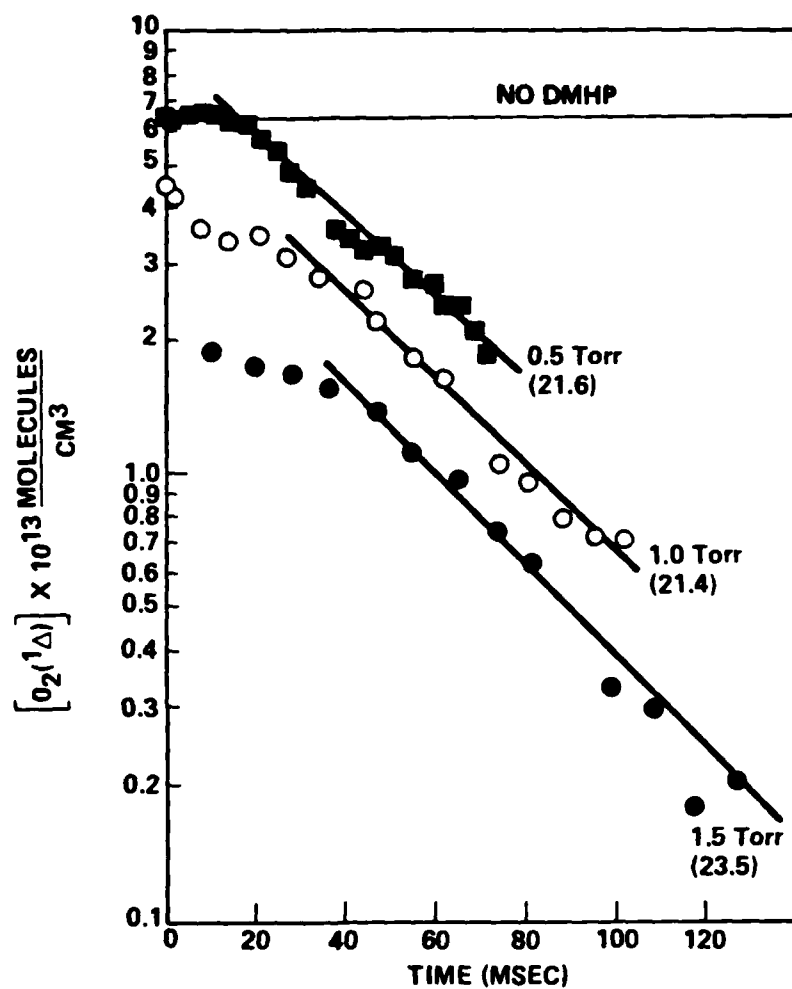
11

Figure 5. Singlet Oxygen Decay with 17 μmoles/sec DMHP.
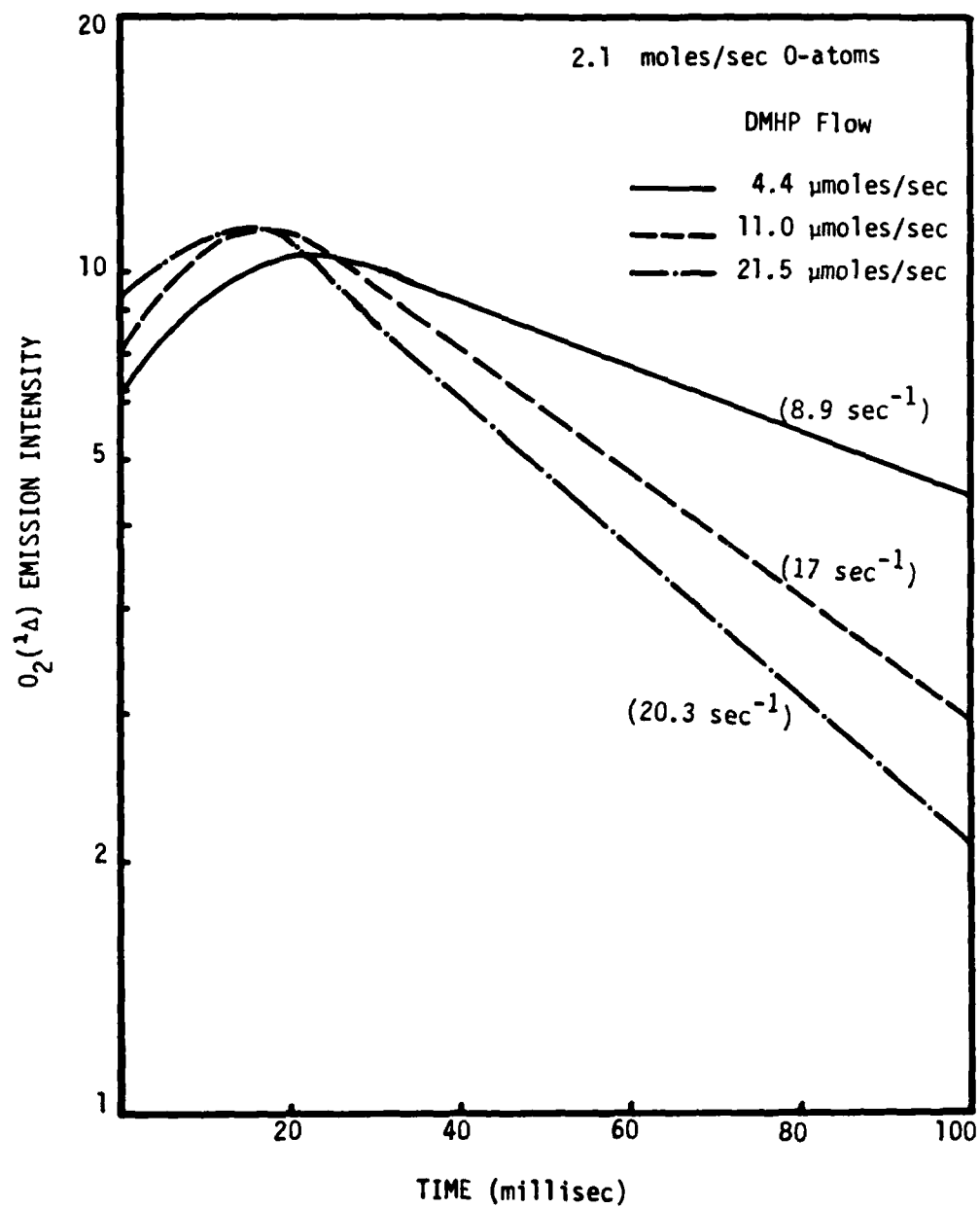1/τ values in parentheses.

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Figure 6. Plots of Singlet Delta Emission Intensity
versus Time for Several DMHP Flowrates.
$1/\tau$ values in parentheses

Table 3. SUMMARY OF EXPERIMENTAL RESULTS WITH DMHP

Pressure (torr)	DMHP (μmoles/ sec)	O (μmoles/ sec)	$O_2(^1\Delta)$ (μmoles/ sec)	Experimental slope (sec^{-1})
0.5	4.4	2.1	2.4	8.9
0.5	11.0	2.1	2.4	17.0
0.5	21.5	2.1	2.4	20.3
0.5	4.4	4.4	4.4*	*
0.5	11.0	4.4	4.4*	13.6
0.5	21.5	4.4	4.4*	23.1
1.0	4.4	5.2	7.8	12.4
1.0	11.0	5.2	7.8	21.2
1.0	21.5	5.2	7.8	29.5
1.0	4.4	2.5	2.2	16.0
1.0	11.0	2.5	2.2	25.2
1.0	21.5	2.5	2.2	25.2

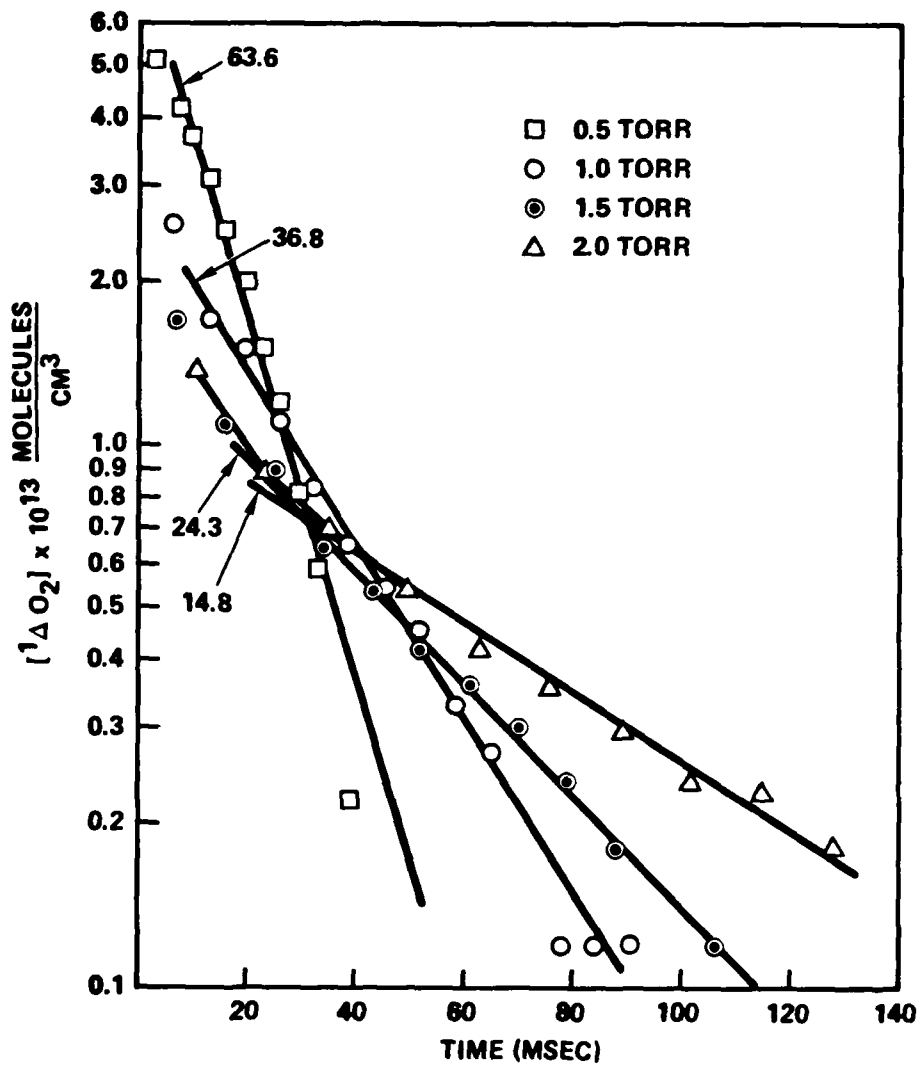*Baseline with no DMHP showed unusual increase which made data reduction difficult.

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Figure 7. Singlet Oxygen Decay with (21.5 μmole/sec) TEP.
1/τ values indicated.
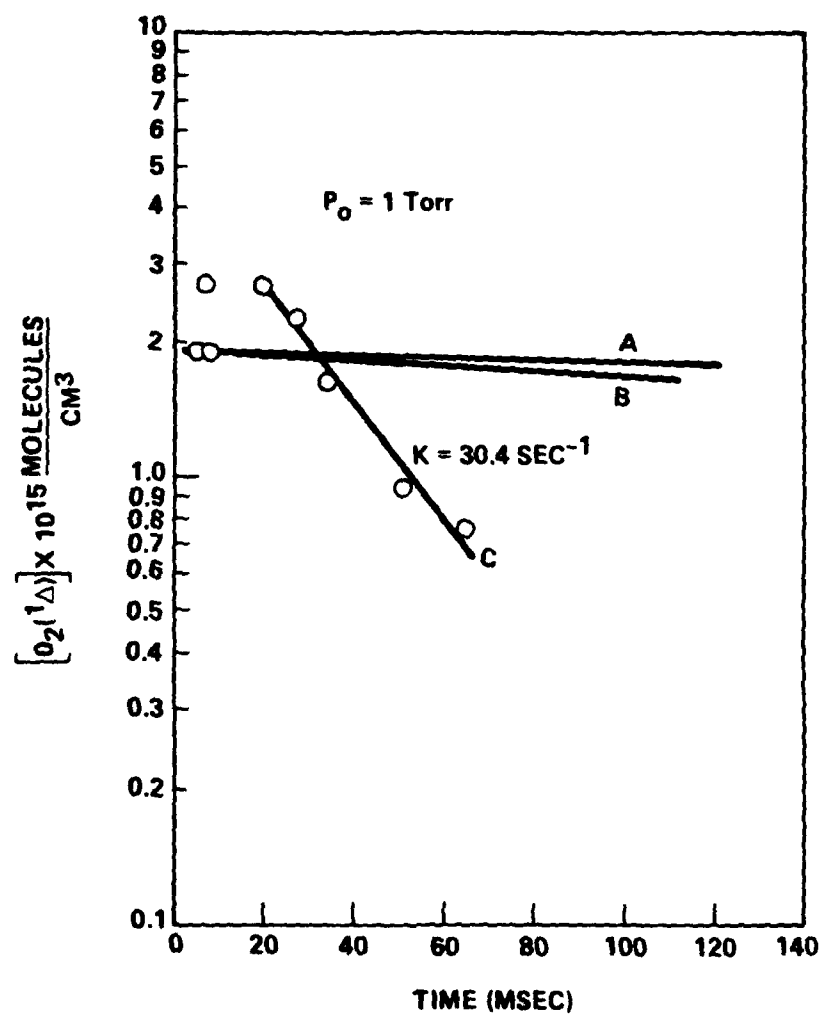
Figure 8. Decay of $O_2{}^1\Delta$ Produced Chemically and With Microwave Discharge in the Presence of DMHP.

A   Chemical Generator Only

B   Chemical Generator + DMHP

C   Chemical and Microwave Generator + DMHP

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The results of the above two series of experiments indicated that some species present in the microwave flow participates in the reaction sequence that leads to quenching of oxygen singlet delta. Addition of NO to the microwave flow between the discharge and mixer resulted in broadband visible emission indicating the presence of oxygen atoms. The NO addition also effectively terminates the quenching of singlet oxygen by P-compounds as is illustrated for DMHP in Figure 9. In a separate experiment, NO_2 was added downstream of the mixer through the sampling ports to test for the presence of O-atoms. There was no detectable broad emission from Reaction (7) and no change in the slope of the 1.27 micron emission versus time when NO_2 was added 15 and 30 cm downstream from the mixer. This is evidence that no significant concentration of O atoms remains in the flow tube downstream of the mixer. This experiment also shows that NO_2 does not terminate the quenching reaction. However, when NO_2 was added 4.5 cm downstream of the mixer, the plots shown in Figure 10 were obtained. The 1.27 micron emission was reduced and the oxygen singlet delta quenching reaction was terminated. In addition, no broadband visible emission was observed. This indicates that the initiation reaction between O atoms and DMHP must be competitive with the reaction between O atoms and NO_2 (Reaction (6)).

Data obtained where oxygen atom concentration was controlled by addition of NO_2 to the flow before the mixer is shown in Figures 11 and 12. In these experiments, the initial enhancement at 1.27 microns was reduced and the quenching of oxygen singlet delta appeared to be stopped. It is postulated that two effects were involved. First, the NO_2 reduced the O-atom concentration resulting in less reaction and second, the NO produced in Reaction (6) terminates the quenching of the oxygen singlet delta.

Experiments to verify the role of NO in the termination reaction were performed. In these experiments, NO was added at ports 10 and 30 cm downstream from the mixer and the 1.27 micron emission decay was observed. The results of these runs are shown in Figures 13 and 14. The addition of NO effectively terminated the oxygen singlet delta quenching. This verified the hypothesis that NO formed in the reaction of O with NO_2 was the species responsible for termination of oxygen singlet delta quenching.
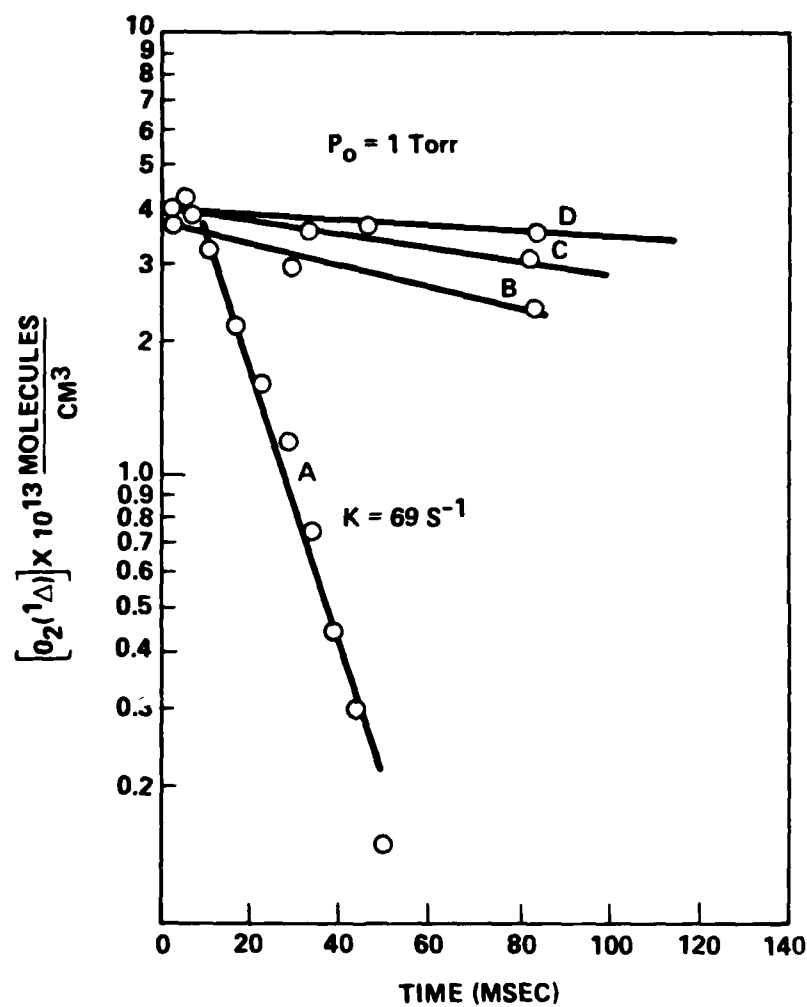
Figure 9. Quenching of $O_2{}^1\Delta$ Inhibited by Addition of NO to Microwave Discharge Flow[2] (0.3 mmoles/sec O_2)

A Microwave with 9.5 μmoles/sec DMHP

B Microwave with DMHP and 0.8 μmoles/sec NO

C Microwave with DMHP and 1.2 μmoles/sec NO
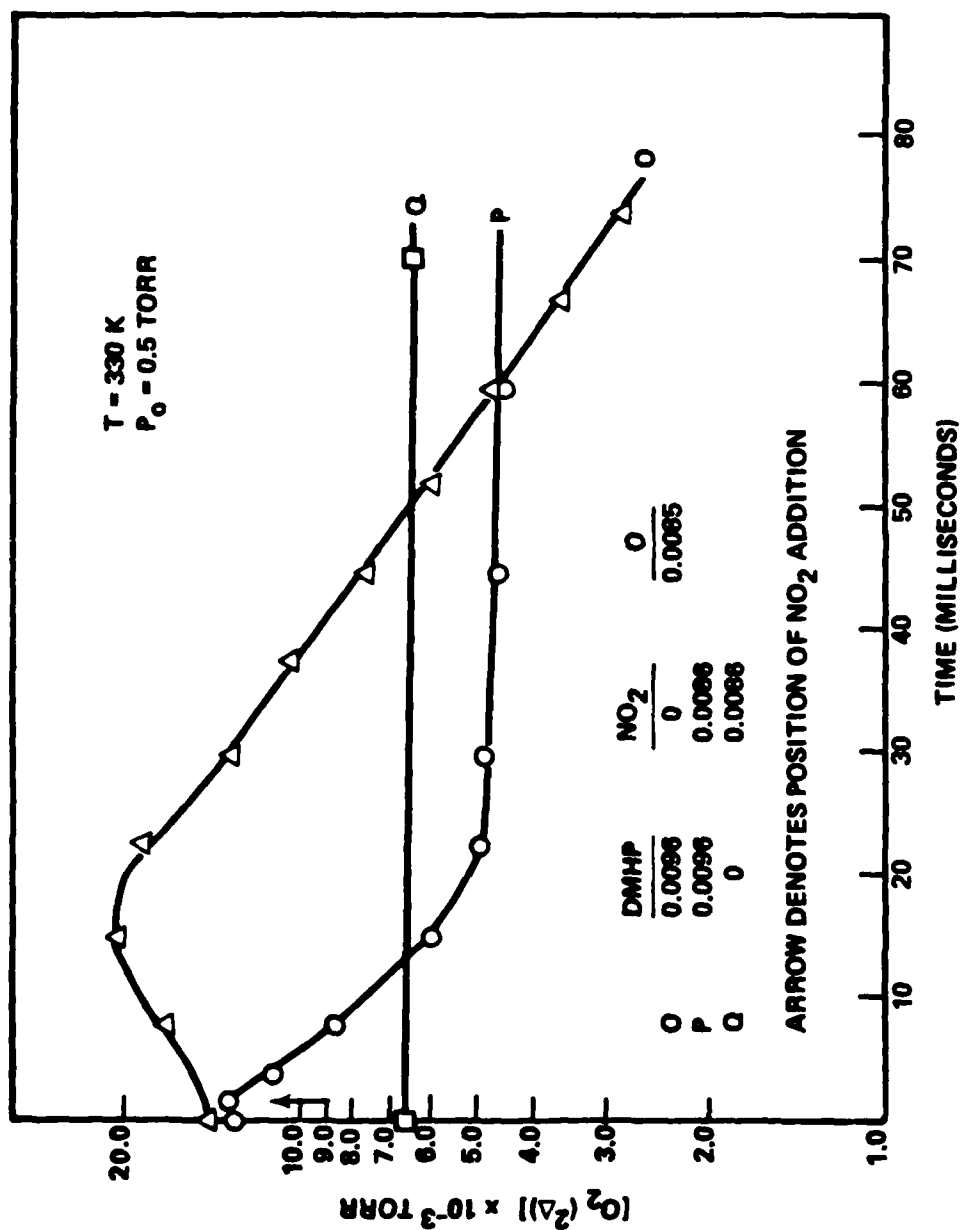
D No DMHP, Microwave Singlet Oxygen Generator

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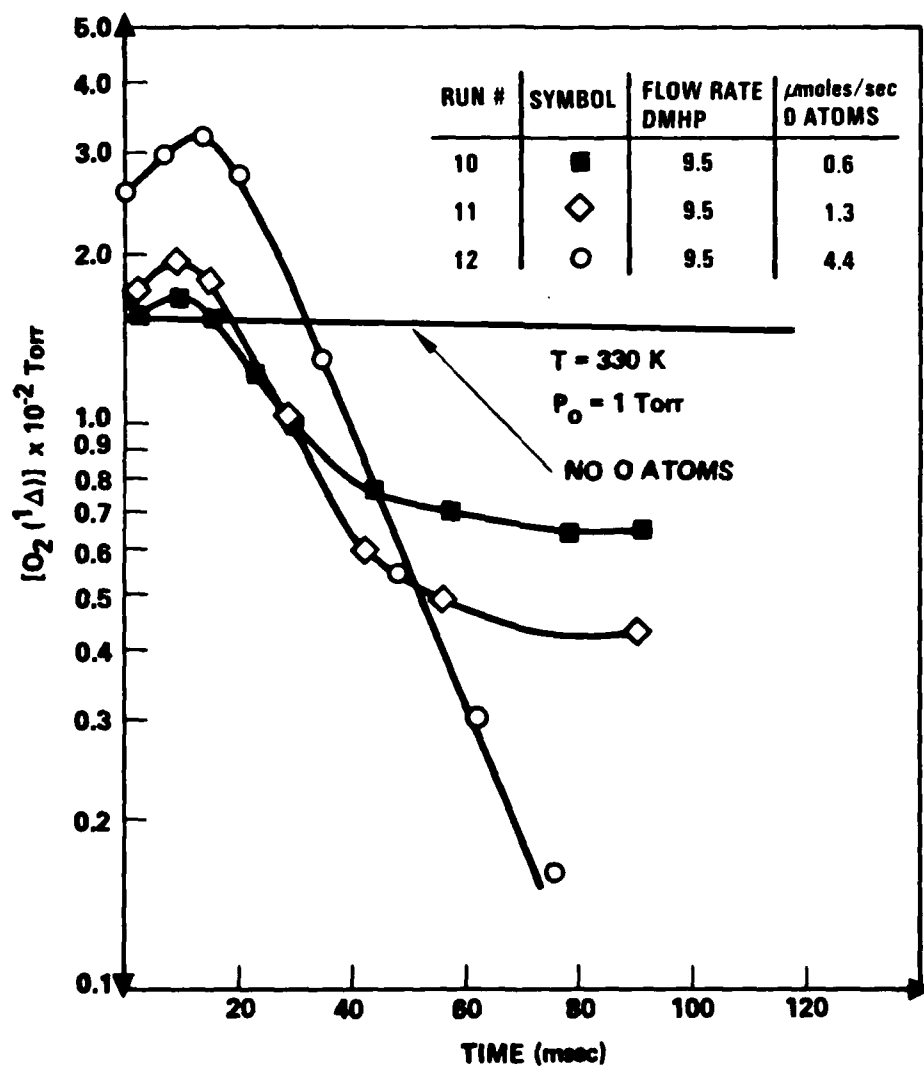Figure 10. Microwave Generated Singlet Oxygen Reaction with DMHP and NO_2 Added 4.5 cm Downstream.

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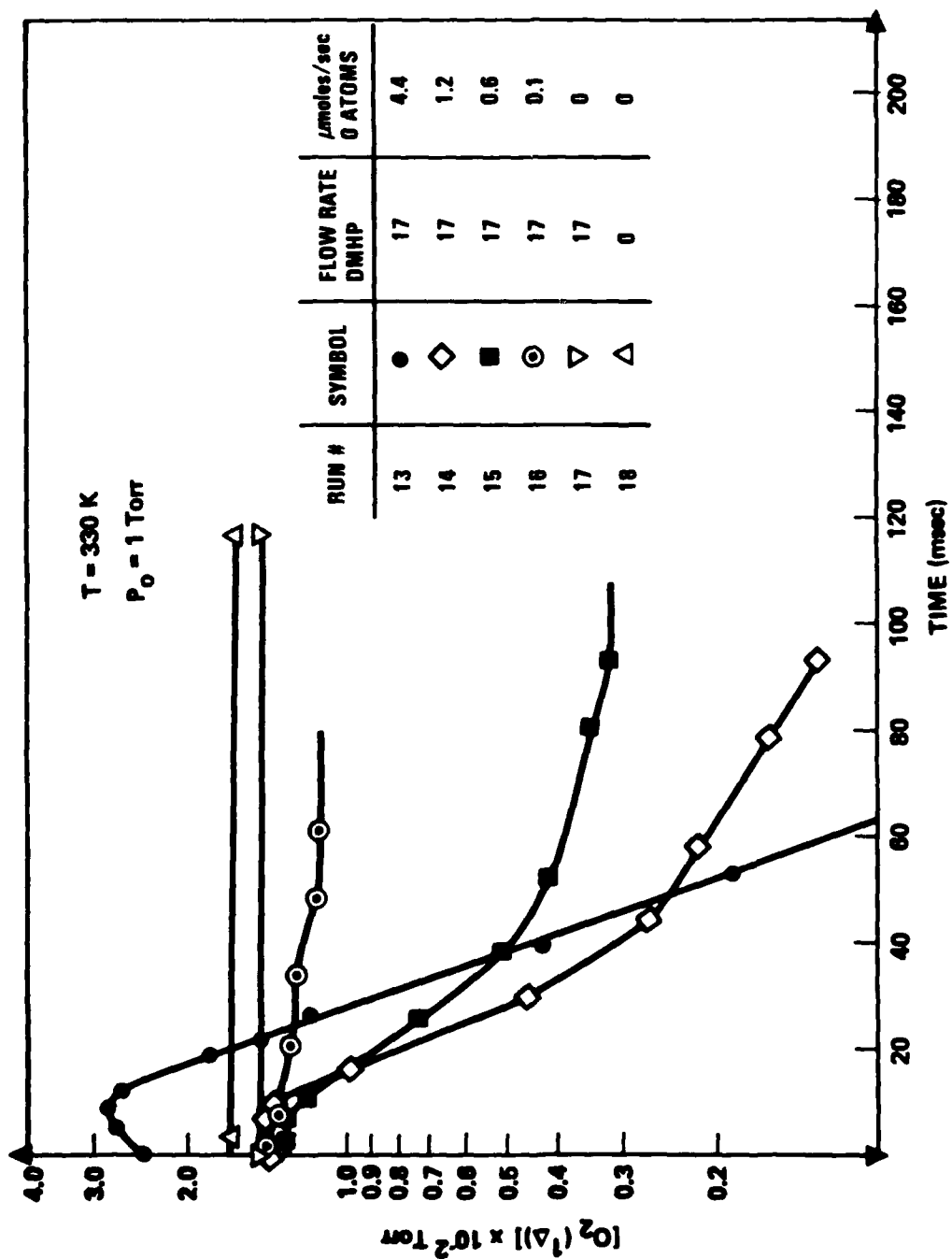Figure 11. Microwave Generated Singlet Oxygen
Reaction with DMHP

Figure 12. Microwave Generated Singlet Oxygen Reaction With DMHP

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$[O_2(^1\Delta)] \times 10^2$ Torr

2.0

no DMHP

1.0

no NO

NO in 1st PORT

0.5

NO IN
2nd PORT

0.2

1st 2nd

INJECTION
PORT

0.1

0.05

0.02

0.01

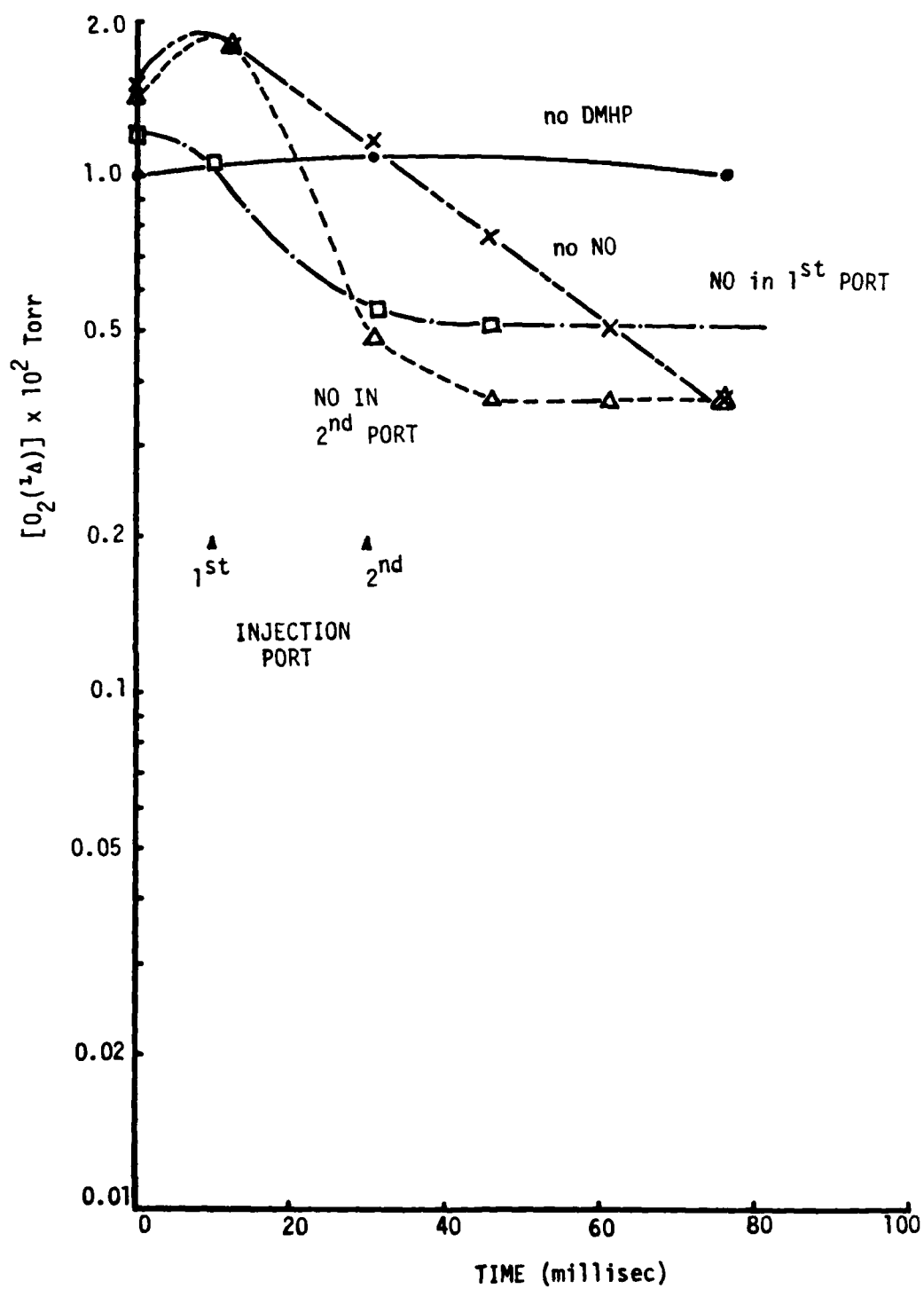0   20   40   60   80   100

TIME (millisec)

Figure 13.   Addition of NO downstream of mixer for 4.5 μmoles/sec DMHP,
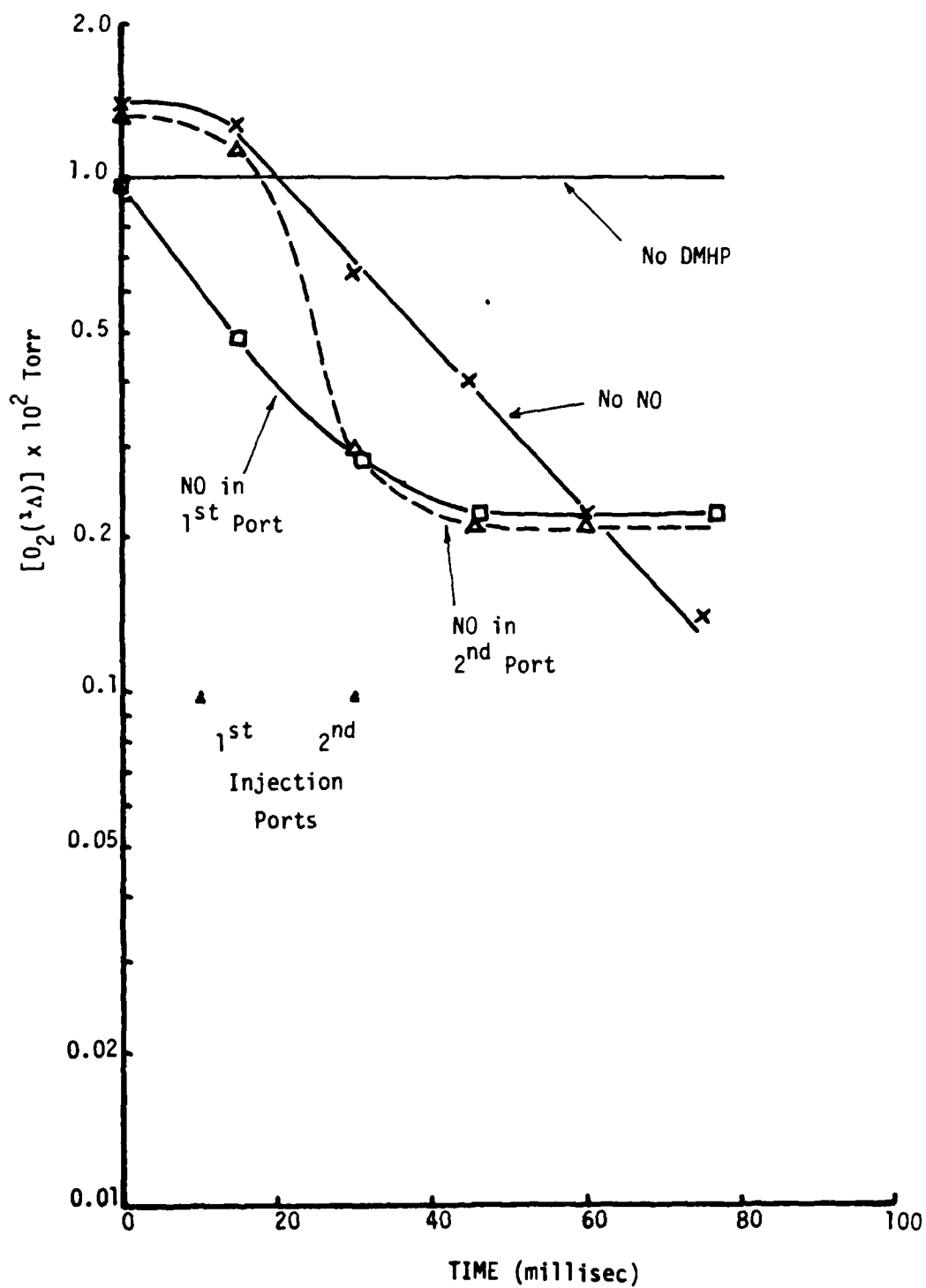2.5 μmoles/sec O-atoms and 2.5 μmoles/sec NO. Pressure = 0.5 Torr.

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Figure 14. Addition of NO downstream of mixer for 9 μmoles/sec DMHP, 2.5 moles/sec O-atoms and 2.5 μmoles/sec NO. Pressure = 0.5 Torr

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Another point of interest was whether the oxygen singlet delta would promote the hydrolysis of the P-compounds. For these experiments, water was added to the flow along with the phosphorus compound. The results of this series of experiments is shown in Figure 15. There appeared to be no change in the slope of the 1.27 micron emission with or without water. This is evidence that the hydrolysis reaction proceeds at a slower rate than the reaction of O atoms with the phosphorus compound.

The enhanced emission at 1.27 microns was examined through the first observation window. Some representative spectra obtained in these experiments are shown in Figure 16. The top two spectra show an increase in the emission when DMHP is added to the flow with O atoms present. There appears to be relatively broadband emission underlying the oxygen singlet delta emission The bottom two spectra show that the removal of O-atoms by NO_2 titration restores the emission profile to that of the pure $O_2(^1\Delta)$ emission spectra.

The origin of this increased emission is uncertain. A likely explanation, which will be discussed later, is that the oxygen singlet delta transfers some energy to the quenching species which then emits at approximately the same wavelength. The time dependence of the different spectral features was monitored with a monochromator/detector set for a 20 Angstrom bandwidth (compared to the 100 Angstrom bandwidth of the filter used to monitor the oxygen singlet delta emission. Wavelengths of 1.272 microns (Peak of P-branch of the $O_2(^1\Delta)$ emission), 1.2682 microns (Peak of the Q-branch of the $O_2(^1\Delta)$ emission) and 1.264 microns (Peak of the R-branch of the $O_2(^1\Delta)$ emission) were chosen. Results are shown in Figure 17. The emission at the P and R branches increases slightly at short distances and then decays. The Q-branch emission shows a constant decay. In addition, emission at wavelengths off the peaks of the oxygen singlet delta emission, 1.254 microns and 1.26 microns, was monitored. These results are shown in Figure 18. The emission at 1.254 microns showed a sharp increase, indicating that this was a new emission. That at 1.26 microns showed an initial increase followed by a slow decay.

Samples of reaction product were collected from the gas phase reaction and from the walls of the flowtube and analyzed with gas chromatography and mass spectrometry. Some of these samples were dissolved in acetronile
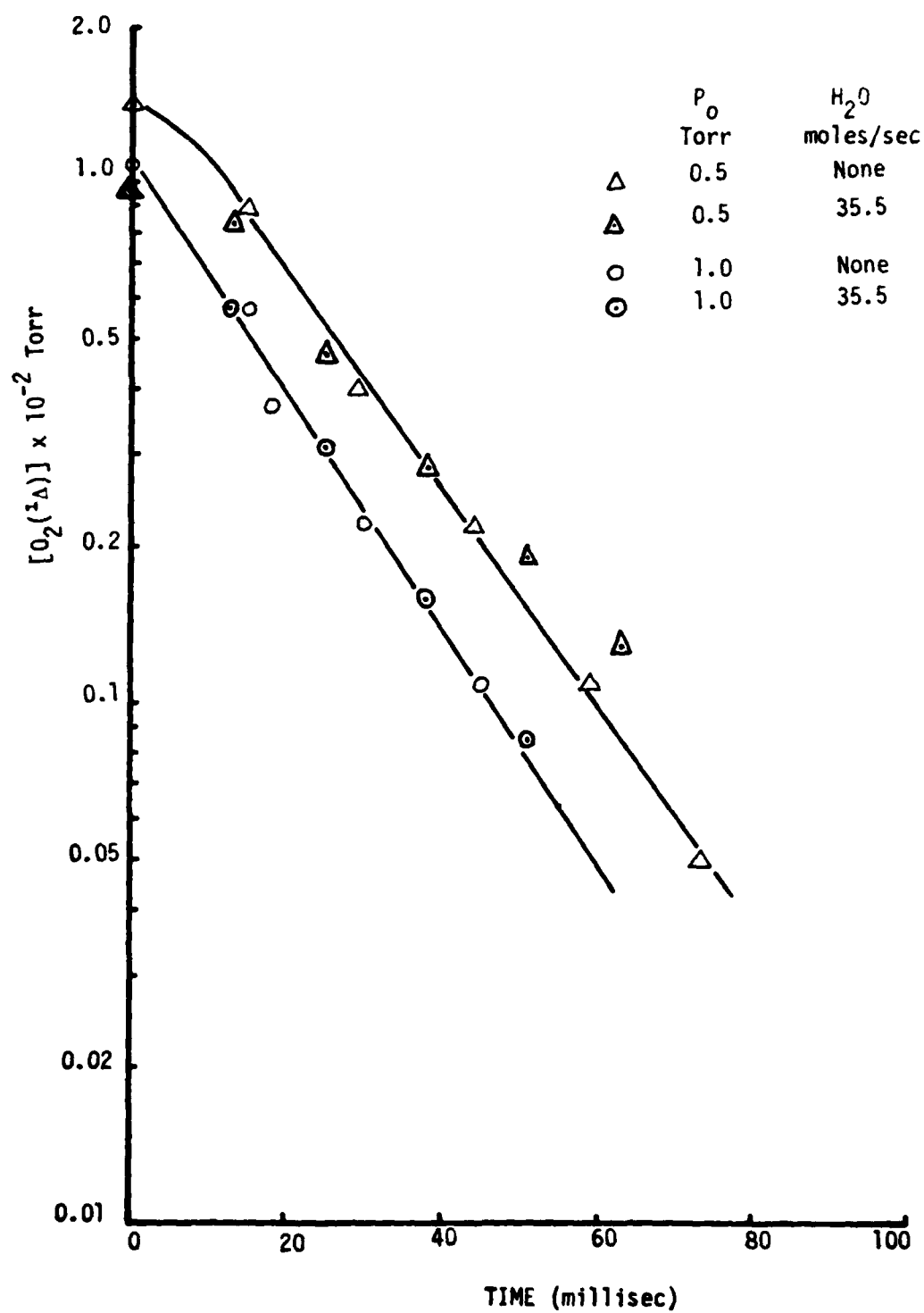
Figure 15. Effect of water addition on $O_2(^1\Delta)$ emission intensity in the presence of 17 μmoles/sec DMHP.
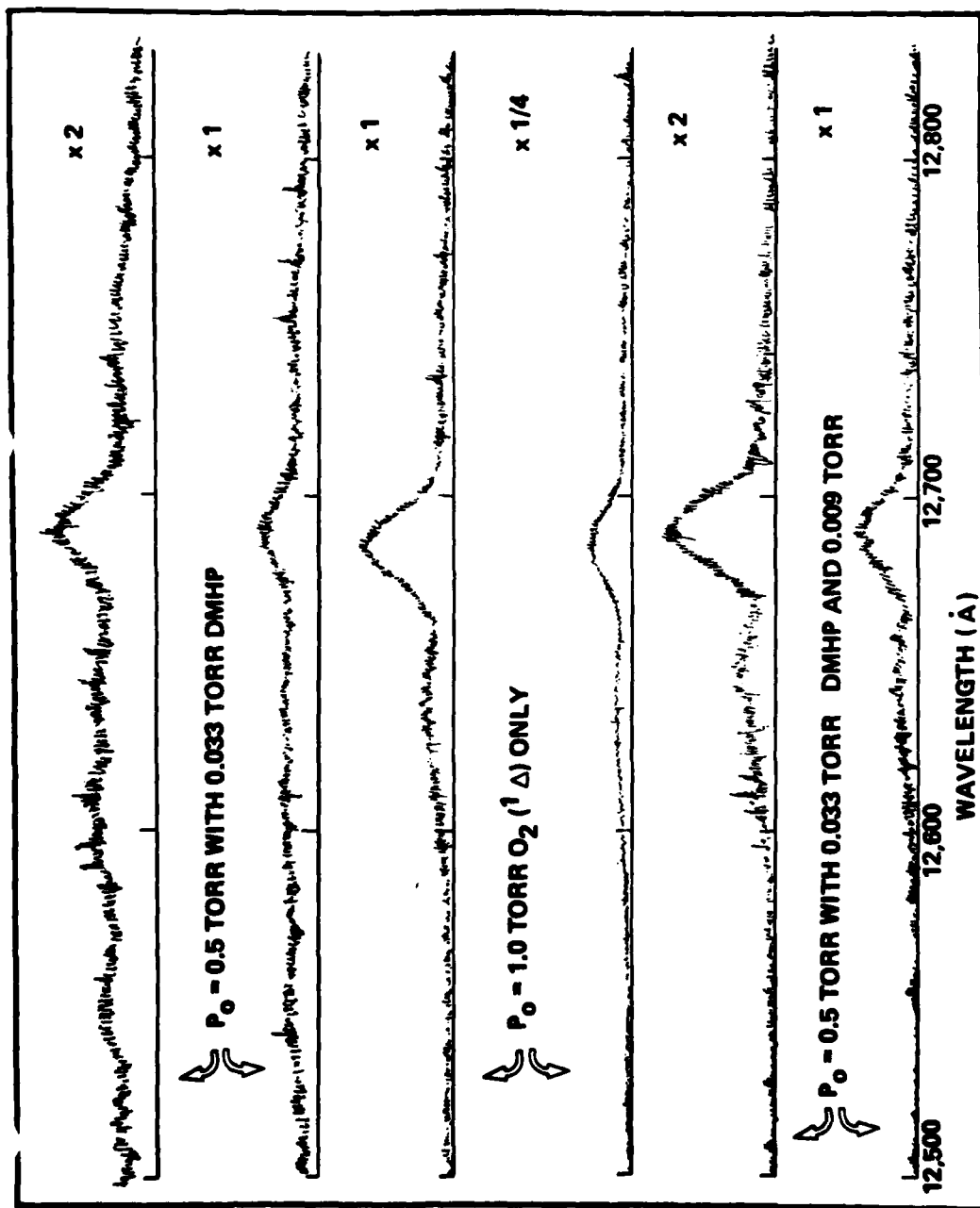
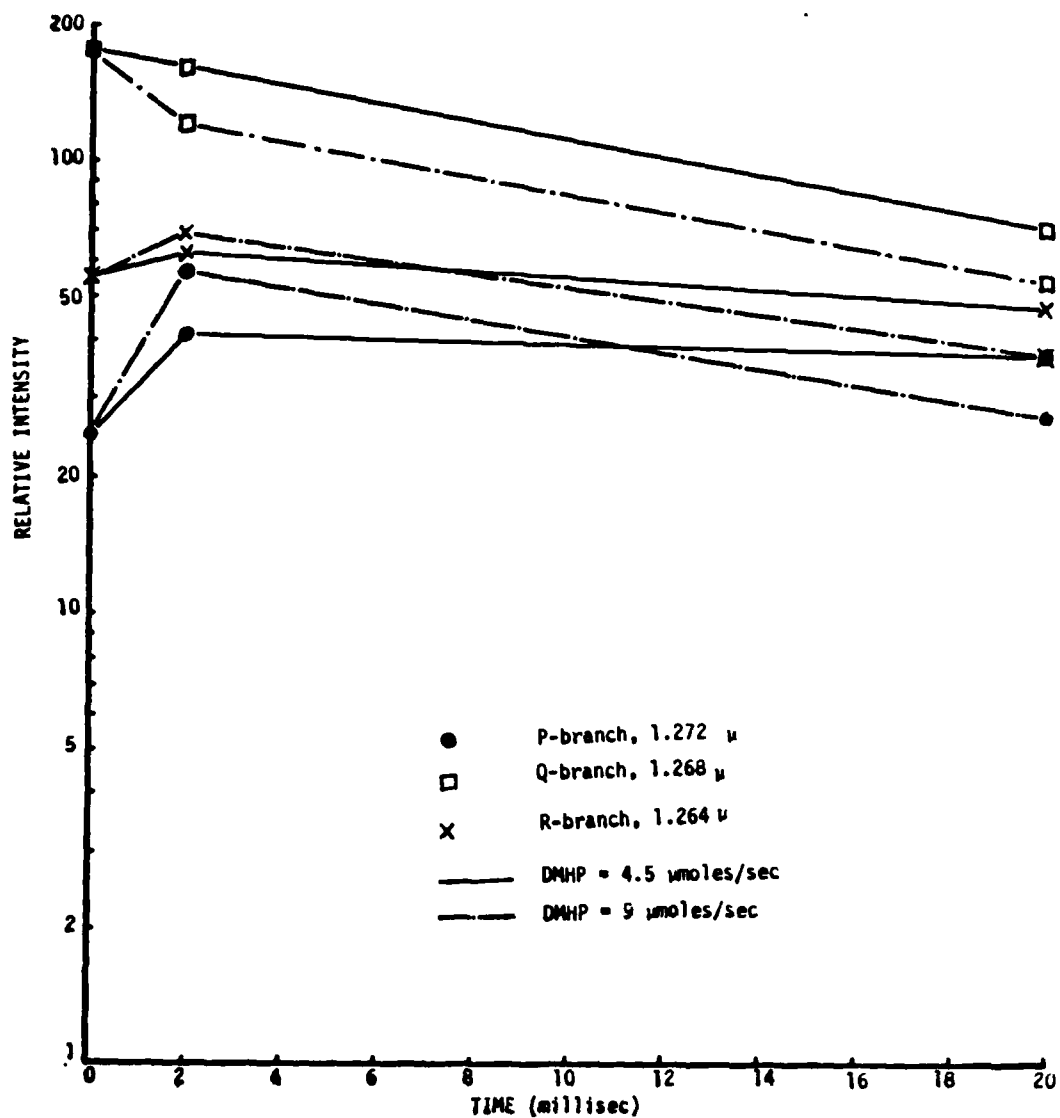Figure 16. $O_2(^1\Delta)$ Emission Spectra

Figure 17. Time dependence of emission at wavelengths corresponding to peaks of P, Q and R branches of $O_2(^1\Delta)$ emission.
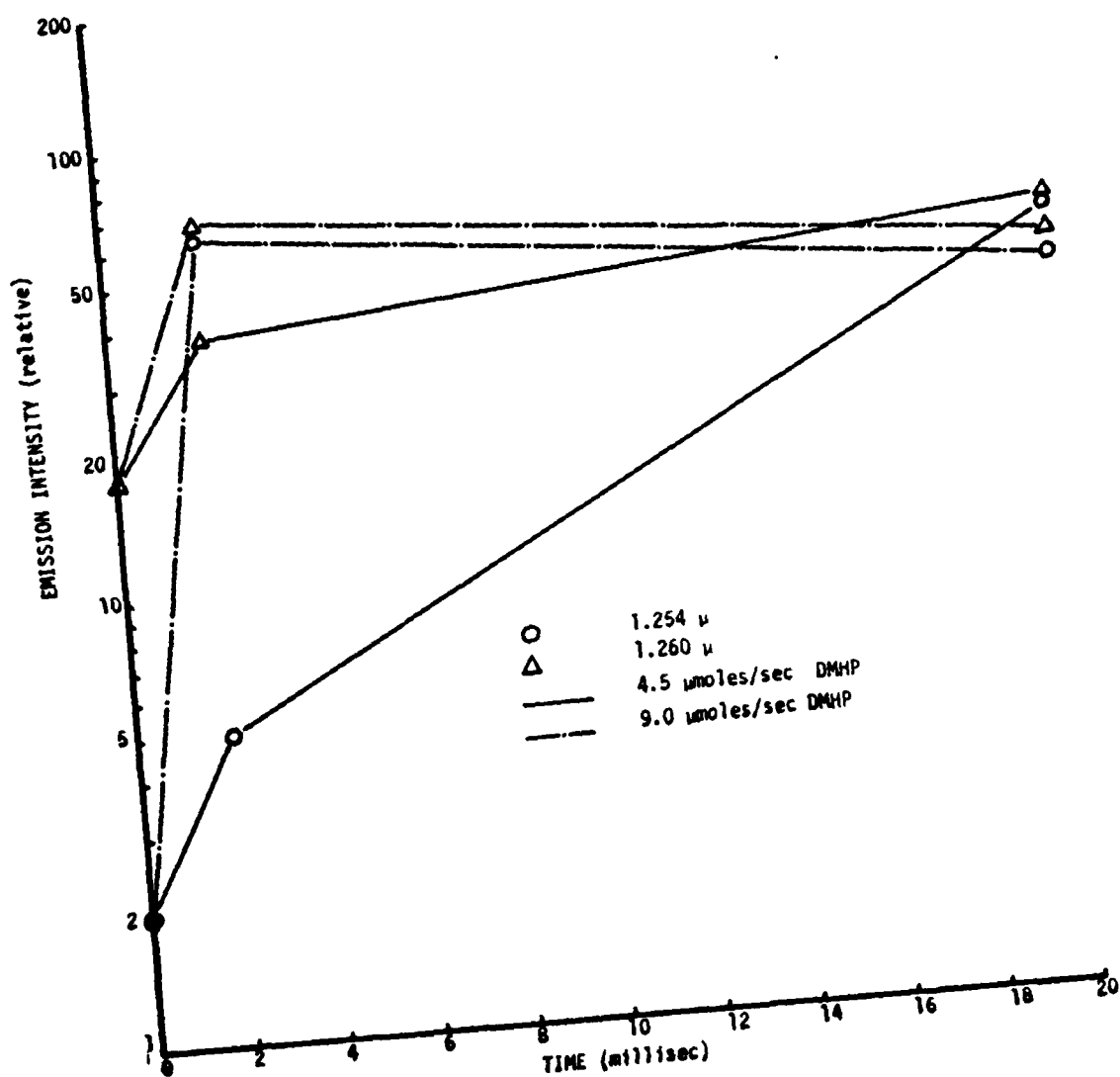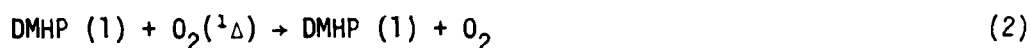
Figure 18. Time dependence of emission intensity at wavelengths 1.25 and 1.26 μ.

and the IR spectra taken. The gas chromatograph indicated that the original sample of DMHP was 98.3% pure and that the impurities were analogs of DMHP. A portion of the IR spectra is shown in Figure 19. Additional absorption occurred in the reaction product near 1200 cm^{-1}. However, the spectral data is not complete enough to determine the structural groups in the products.

3.3 DISCUSSION OF RESULTS

The major features of the experiment that need to be explained are the role of oxygen atoms in the reaction sequence, the enhanced emission at 1.27 microns that is observed upon addition of DMHP to the flow, and the linear decay of the 1.27 micron emission. In addition, the results with NO and NO_2 need a qualitative explanation. The type of mechanism which best explains the experimental results is detailed below:

$$O + DMHP \rightarrow DMHP~(1) \tag{1}$$

$$DMHP~(1) + O_2(^1\Delta) \rightarrow DMHP~(1) + O_2 \tag{2}$$

$$DMHP~(2) + O_2(^1\Delta) \rightarrow DMHP~(2) + O_2 \tag{3}$$

$$DMHP~(2) \rightarrow DMHP~(1) + h\nu \tag{4}$$

$$DMHP~(1) + NO \rightarrow DMHP~(3) \tag{5}$$

The individual reactions are discussed in more detail below.

REACTION 1: All experimental observations indicate that oxygen atoms are necessary to initiate any quenching of the oxygen singlet delta. Using what is known about the chemistry of pentavalent phosphorus, the most likely place for the oxygen to attack is the P = O bond forming a complex in which 5 atoms (4 O-atoms and one H-atom) are bonded to the phosphorus. This species may be stable for the lifetime of the flowtube experiments (100 msec). The rate of this reaction is probably of the order of the reaction of O-atoms with NO_2 since experimental observations have shown O-atoms are depleted soon after the DMHP is mixed with the flow.

REACTIONS 2 and 3: These two reactions give an overall rate for quenching of oxygen singlet delta by the intermediate phosphorus compound, DMHP (1). A possible mechanism for the quenching is energy transfer of the energy of the oxygen singlet delta to the DMHP (1) compound with subsequent
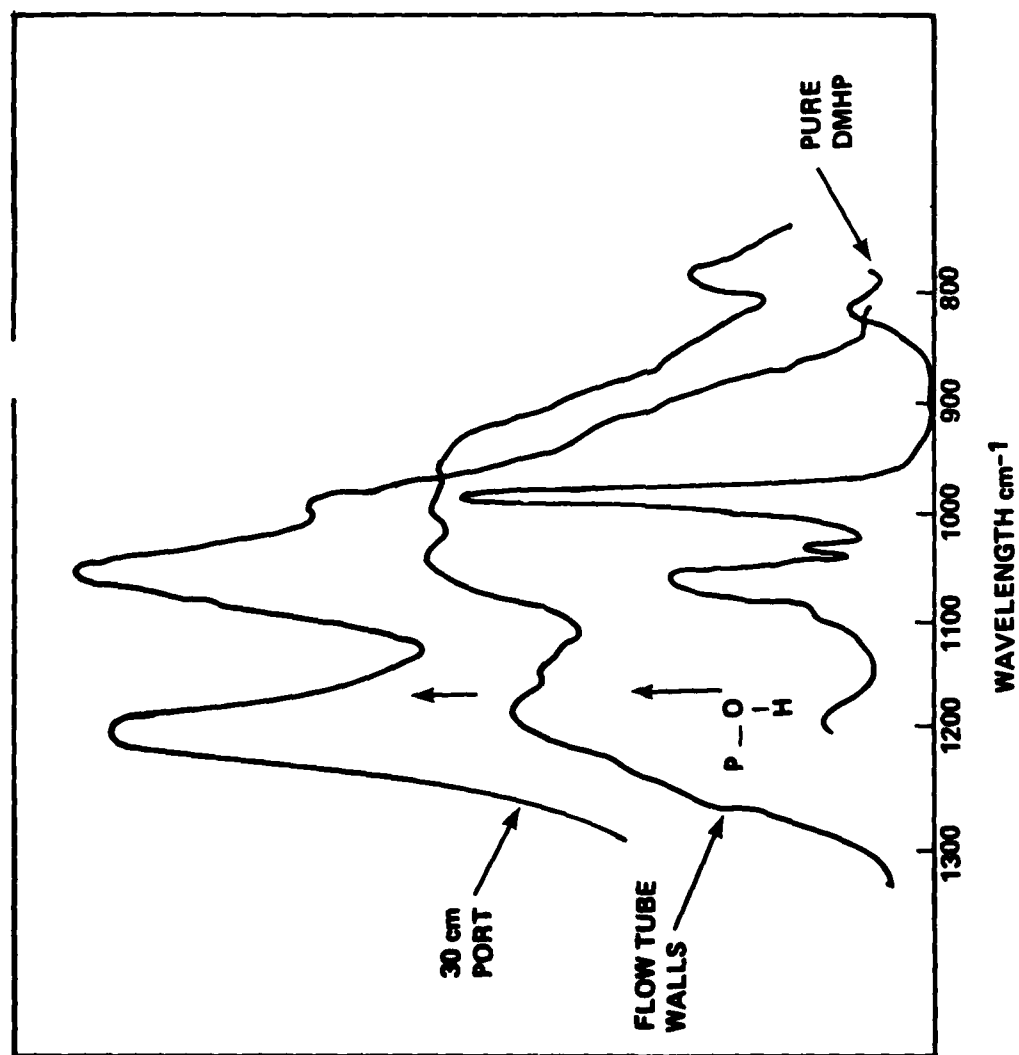
29

Figure 19. IR Absorption Spectra of DMHP Samples

quenching and/or radiation from this compound. Kinetically, formation
of an intermediate excited species which either radiates or decays to
the original species gives will explain the experimental result as well
as a mechanism with straight quenching and no energy transfer. There is
evidence that the quenching reaction regenerates a quenching species
since there is a linear decay and many singlet delta molecules can be
quenched by one molecule of the quenching species.

REACTION 4: Reaction (3) followed by Reaction (4) is needed to explain
the enhanced emission at 1.27 microns which is observed at short distances
in the flow tube. If energy is transferred from oxygen singlet delta,
it is not unreasonable that a small amount is reemitted at approximately
the same wavelength. The fraction of energy channelled via Reactions (3)
and (4) can be very small and still model the experimental results. The
time dependent spectra at different wavelengths tend to support this
hypothesis. When only the peak of the Q-branch emission was monitored,
a monotonic decrease in the emission was observed. However, emission
off the peak showed an increase in intensity at short times. Thus, it
is possible that the emission monitored through the 100 Angstrom bandwidth
filter consisted of a combination of these two features, explaining the
enhanced emission.

REACTION 5: The ability of the intermediary phosphorus compound to
quench singlet oxygen appears to be removed by Reaction (5). This was
substantiated by experiments in which NO was added downstream of the
phosphorus compound and cessation of quenching observed.

A kinetic model based on the above reaction mechanism was used to
model the experimental data. A sample run for a case with no NO or
NO_2 is shown in Figure 20. The rates used to fit this data set are shown
in Table 4. Note that a very small branching ratio into the emitting
species is needed to explain the experimental results. It was not
possible to model all the experimental data with the same set of rates.
The model showed less dependence on the DMHP concentration when the DMHP
was in excess than shown by the experiments. Modeling with NO qualitatively
shows the quenching of oxygen singlet delta leveling off. However, a
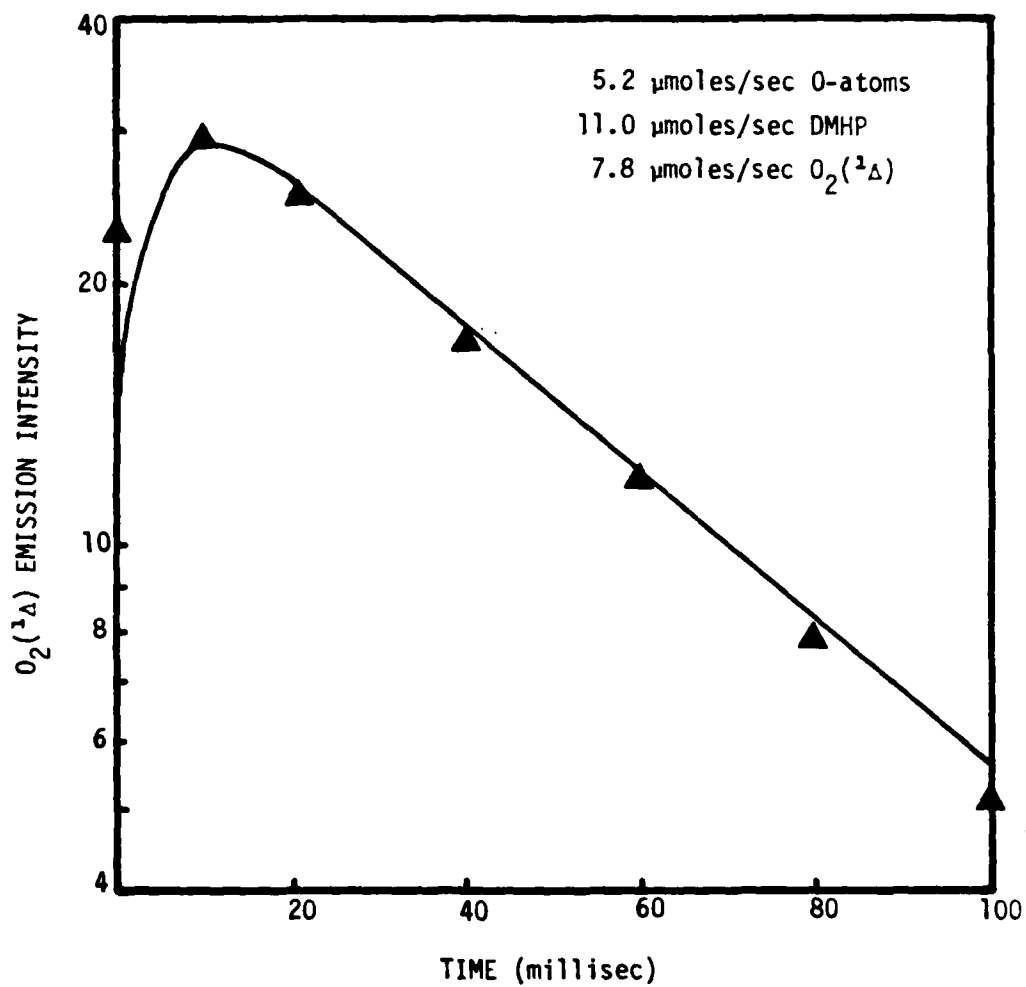quantitative fit was not obtained.

Figure 20. Comparison of code and experiment. Points are
experimental data, line is code prediction.

Table 4. REACTION MECHANISM AND RATES

REACTION	RATE $(cm^3 \ molecule^{-1} \ sec^{-1})$
$O + DMHP \rightarrow DMHP \ (1)$	1.0×10^{-12}
$DMHP \ (1) + O_2(^1\Delta) \rightarrow O_2 + DMHP \ (1)$	6.0×10^{-14}
$DMHP \ (1) + O_2(^1\Delta) \rightarrow O_2 + DMHP \ (2)$	1.0×10^{-18}
$DMHP \ (2) \rightarrow DMHP \ (1) + h\nu$	1.0×10^{6}

The experiments in which water was added to the flow tube indicated that the hydrolysis of DMHP is a slow reaction which is not appreciably enhanced by the presence of oxygen singlet delta. This data indicates that the rate of the hydrolysis reaction is less than 10^{-14} cm^3 molecule^{-1} sec^{-1}.

The IR spectra allow some speculation about the structure of the intermediate species. Note that there is enhanced emission in the range 1300-1100 cm^{-1} which is normally assigned as a P-O frequency. This would tend to support the hypothesis that an oxygen atom reacts to form an additional P-O bond and also changes the nature of the existing P = O bond. A second hypothesis that the collected samples are hydrolysis products was not conclusively eliminated.

4.0 PERSONNEL

Dr. L. J. Marabella was the principal investigator on this effort Dr. J. Kuper and Mr. C. Lovejoy assisted by Mr. A. Edmon collected most of the experimental data. Dr. J. Betts aided in data analysis and kinetic modeling.